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(54) Title: METHOD FOR MANUFACTURING AROMATIC CARBOXYLIC ACID

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(57) Abstract

Purpose: To provide a method that greatly reduces the loss due to the combustion of a reaction medium and freely adjusts the content of an aromatic aldehyde in crude aromatic carboxylic acid crystals, when an aromatic carboxylic acid is manufactured by a liquid-phase oxidizing reaction of an aldehyde aromatic hydrocarbon.

Solution means: In a method that manufactures an aromatic carboxylic acid by subjecting an alkyl aromatic hydrocarbon to a liquid-phase oxidation by a gas containing molecular oxygen in the presence of a catalyst containing cobalt, manganese, and bromine in a liquid reaction medium, a reaction-medium aromatic carboxylic acid slurry generated in a first oxidation reactor, in which the oxidizing reaction temperature is set to 140-180°C, is subjected to a second oxidation treatment in a second oxidation reactor held at a temperature of 140-190°C for a residence time attained by a specific calculation equation based on the aromatic aldehyde content in the aromatic carboxylic acid crystals in the first oxidation reactor without supplying the alkyl aromatic hydrocarbon.

#### Claims

1. A method for manufacturing an aromatic carboxylic acid, characterized by the fact that in a method for manufacturing an aromatic carboxylic acid by subjecting an alkyl aromatic hydrocarbon to a liquid-phase oxidation in the presence of a catalyst containing cobalt, manganese, and bromine in a liquid reaction medium by a gas containing molecular oxygen: (1) the oxidizing reaction temperature in a first oxidation reactor is set to 140-180°C; (2) a reaction-medium aromatic carboxylic acid slurry generated in the first oxidation reactor in the above-mentioned method (1) is subjected to a second oxidation treatment in a second oxidation reactor held at a temperature of 140-190°C for the following residence time without supplying the alkyl aromatic hydrocarbon.

“ Second oxidation reactor residence time”: The calculated value in which 3,000 is substituted for (B) in the following equation is assumed as the minimum value, and the calculated value in which 1,500 is substituted is assumed as the maximum value.

(Expression 1) Second oxidation reactor residence time (min) =  
(purification coefficient)  $\times ((A) - (B)) / (B)$

Where, (A) represents the aromatic aldehyde content (ppm unit) in the aromatic carboxylic acid crystals in the first oxidation reactor. When (A) is larger than 4,500 ppm, the purification coefficient is 33; when (A) is 3,000-4,500 ppm, the purification coefficient is 50; and when (A) is smaller than 3,000 ppm, the purification coefficient is 100. However, if the value in which 3,000 is substituted for (B) is negative, the minimum value of the second oxidation reactor residence time is set to 0 min, and if the value in which 1,500 is substituted for (B) is negative, the second oxidizing reaction is not carried out.

2. The method for manufacturing an aromatic carboxylic acid of Claim 1, characterized by the fact that the aromatic aldehyde content in the aromatic carboxylic acid crystals after the oxidation treatment in the second oxidizing reaction is 1,500-3,000 ppm.

3. The method for manufacturing an aromatic carboxylic acid of Claim 1, characterized by the fact that the second oxidation is carried out for a residence time obtained by respectively substituting the minimum value (ppm units, but 1,500 ppm or more) and the maximum value (ppm units, but 3,000 ppm or less) of the desired level of the aromatic aldehyde -- after the oxidation treatment in the second oxidation reactor -- for (B) in the equation.

#### Detailed explanation of the invention

[0001]

#### Technical field of the invention

The present invention pertains to a method for manufacturing an aromatic carboxylic acid. Specifically, the present invention pertains to a method for manufacturing an aromatic carboxylic acid that can freely adjust the content of an aromatic aldehyde in crude aromatic carboxylic acid crystals, while largely preventing the combustion loss of acetic acid as a reaction medium in a liquid-phase oxidizing reaction of an alkyl aromatic hydrocarbon, which manufactures crude aromatic carboxylic acid crystals.

[0002]

#### Prior art

As a method for manufacturing an aromatic carboxylic acid such as terephthalic acid, industrially, a method that subjects an alkyl aromatic hydrocarbon such as para-xylene to a

liquid-phase oxidizing reaction with molecular oxygen in the presence of a catalyst containing cobalt, manganese, and bromine in an acetic acid solvent is generally used. As an example, when terephthalic acid is obtained by subjecting para-xylene to a liquid-phase oxidation by the above-mentioned method, usually, 4-carboxybenzaldehyde (hereinafter, abbreviated as "4CBA") as one of the reaction intermediates, or a large amount of impurities generated by a side reaction, is included in said terephthalic acid. Therefore, said terephthalic acid has been used as polyester raw material, etc., only after applying a purification treatment to it. As such a purification method, a method that applies a hydrogenation treatment or an oxidation treatment to crude terephthalic acid is known. Of these methods, as the hydrogenation purification method, a method that reduces an aqueous solution of crude terephthalic acid at high temperature and high pressure in the presence of a hydrogenation catalyst and that recovers terephthalic acid crystals from the aqueous solution treated is proposed (see Japanese Kokoku Patent No. Sho 41[1966]-16860).

[0003]

Problems to be solved by the invention

Usually, the quality of the aromatic carboxylic acid such as terephthalic acid obtained by the liquid-phase oxidizing reaction of an alkyl aromatic hydrocarbon such as para-xylene can be adjusted by appropriately selecting the reaction conditions such as the temperature of said oxidation reactor, the amount of catalyst used, and residence time. For example, in order to reduce the content of an aromatic aldehyde such as 4CBA, generally, the reaction temperature or catalyst concentration is raised, so that the oxidizing reaction conditions become strict. However, under these conditions, since the reaction medium such as acetic acid is easily combusted or decomposed as a side reaction, the amount of reaction medium being lost is increased, and the manufacturing cost of the aromatic carboxylic acid is raised. On the contrary, in said oxidizing reaction, if the reaction temperature is set low to prevent the loss of the reaction medium due to the above-mentioned side reaction, the activity of the main reaction is also lowered, so that the content of the aromatic aldehyde existing in the aromatic carboxylic acid obtained is increased. The present invention provides a method that greatly reduces the loss due to the combustion of a reaction medium and freely adjusts the content of aromatic aldehyde in crude aromatic carboxylic acid crystals.

[0004]

Means to solve the problems

In other words, the essence of the present invention is a method for manufacturing an aromatic carboxylic acid, characterized by the fact that in a method for manufacturing an aromatic carboxylic acid by subjecting an alkyl aromatic hydrocarbon to a liquid-phase oxidation in the presence of a catalyst containing cobalt, manganese, and bromine in a liquid reaction

medium by a gas containing molecular oxygen: (1) the oxidizing reaction temperature in a first oxidation reactor is set to 140-180°C; (2) a reaction-medium aromatic carboxylic acid slurry generated in the first oxidation reactor in the above-mentioned method (1) is subjected to a second oxidation treatment in a second oxidation reactor held at a temperature of 140-190°C for the following residence time without supplying the alkyl aromatic hydrocarbon.

“Second oxidation reactor residence time”: The calculated value in which 3,000 is substituted for (B) in the following equation is assumed as the minimum value, and the calculated value in which 1,500 is substituted is assumed as the maximum value.

[0005]

(Expression 2) Second oxidation reactor residence time (min) =  
(purification coefficient)  $\times ((A) - (B)) / (B)$

[0006] Where, (A) represents the aromatic aldehyde content (ppm units) in the aromatic carboxylic acid crystals in the first oxidation reactor. When (A) is larger than 4,500 ppm, the purification coefficient is 33; when (A) is 3,000-4,500 ppm, the purification coefficient is 50; and when (A) is smaller than 3,000 ppm, the purification coefficient is 100. However, if the value in which 3,000 is substituted for (B) is negative, the minimum value of the second oxidation reactor residence time is set to 0 min, and if the value in which 1,500 is substituted for (B) is negative, the second oxidizing reaction is not carried out.

[0007]

#### Embodiment of the invention

Next, the present invention is explained in detail. In the present invention, the alkyl aromatic hydrocarbon used as a raw material is an aromatic hydrocarbon such as mono-, di-, and trialkylbenzene or mono-, di-, and trialkylnaphthalene, being converted into an aromatic carboxylic acid such as aromatic monocarboxylic acid, aromatic dicarboxylic acid, and aromatic tricarboxylic acid by a liquid-phase oxidation, and also includes an aromatic hydrocarbon in which one of the alkyl groups is oxidized. As the alkyl aromatic hydrocarbon, para-xylene, meta-xylene, ortho-xylene, trimethylbenzene, toluene, methylnaphthalene, dimethylnaphthalene, etc., can be mentioned. Also, as the aromatic carboxylic acid being generated, terephthalic acid, isophthalic acid, orthophthalic acid, trimellitic acid, benzoic acid, naphthoic acid, naphthalenedicarboxylic acid, etc., can be mentioned. In the method of the present invention, a dialkyl aromatic hydrocarbon such as para-xylene is preferably used as a raw material for the manufacture of an aromatic dicarboxylic acid such as naphthalenedicarboxylic acid. More preferably, para-xylene or dimethylnaphthalene is used as a raw material for the manufacture of terephthalic acid or naphthalenedicarboxylic acid. Especially preferably, para-xylene is used as a raw material for the method for manufacturing terephthalic acid.

[0008] As the reaction medium of a liquid in said liquid-phase oxidation, usually a lower aliphatic carboxylic acid is used. Acetic acid is especially preferable. Next, the case wherein acetic acid is used as a solvent is explained as an example. The amount of acetic acid solvent used is usually 2-6 weight times that of the alkyl aromatic hydrocarbon. Also, in said acetic acid solvent, a slight amount, such as 10 wt% or less, of water may also be included. As the gas containing molecular oxygen, air, oxygen diluted with an inert gas, oxygen-enriched air, etc., are used, but air is usually used in terms of facility [practicality] and cost.

[0009] The catalyst used in the liquid-phase oxidation generally includes cobalt, manganese, and bromine; as detailed examples, cobalt acetate, cobalt naphthenate, cobalt bromide, etc., can be mentioned as the cobalt compounds. As the manganese compounds, manganese acetate, manganese naphthenate, manganese bromide, etc., can be mentioned, and as the bromide compounds, hydrogen bromide, sodium bromide, cobalt bromide, manganese bromide, tetrabromoethane, etc., can be mentioned. These compounds may also be used in combinations.

[0010] The amount of catalyst used is usually 400-3,000 wt ppm, preferably 500-2,000 wt ppm, in relation to the acetic acid as calculated in terms of cobalt metal. The amount of manganese component used is 0.001-0.4 times the atomic ratio of cobalt. Also, the absolute amount of manganese component used is usually 1-250 wt ppm, preferably 5-200 wt ppm, in relation to the acetic acid as calculated in terms of manganese metal. The amount of bromine component used is 0.1-5 times, preferably 0.2-2.0 times, the atomic ratio of cobalt. If the amount of catalyst used is out of the above-mentioned range, the purity or permeability of the aromatic carboxylic acid obtained is insufficient, or the acetic acid combustion is increased, so that the effect tends to be difficult to obtain. In particular, the amount of manganese component used is important; if the atomic ratio in relation to the cobalt is less than 0.001 times, the reactivity is greatly lowered, and if the atomic ratio is more than 0.4 times, a precipitate of the manganese component is generated and mixed into the aromatic carboxylic acid, so that the quality of the aromatic carboxylic acid as a product is deteriorated, or the loss of acetic acid is increased.

[0011] The reaction is preferably applied under a reaction temperature of the liquid-phase oxidation in the first oxidation reactor of usually 140-180°C, preferably 150-175°C. If the reaction temperature is lower than 140°C, the reaction speed is lowered, and if the reaction temperature is higher than 180°C, the amount of loss due to the combustion of the acetic acid solvent is increased, which is not preferable. The reaction pressure is that at which the mixture can retain the liquid phase at at least the reaction temperature, and it is usually 0.2-5 MPa or higher.

[0012] The reaction is usually continuously carried out, and the residence time is 30-300 min. "Residence time" means the average time of the solid and liquid components spent in the reactor for the reaction. For example, when terephthalic acid is manufactured by subjecting para-xylene

to a liquid-phase oxidation in acetic acid while constantly maintaining the solid and liquid component volume in the reactor by providing a liquid-surface control valve, etc., the average residence time can be calculated as follows. In said reaction, since a slurry of the terephthalic acid is generated, the amount of said slurry being extracted per unit time from the reactor and the amount of slurry held in said reactor (the amount of slurry held) are attained, and the above-mentioned amount of slurry held is divided by the amount of slurry extracted per unit time. This value is adopted as the average residence time. In calculating the amount of slurry per unit time, the total value of the amount of terephthalic acid actually obtained and the amount of reaction medium separated from said terephthalic acid, or the mass balance of the reaction, can be used. The amount of slurry held can be detected from the indicated value of a liquid-surface gauge installed in the reaction chamber. The residence time is controlled to the desired value by adjusting the amount of slurry held in the reactor, the amount of substances introduced into the reactor, etc.

[0013] The reactor used in the present invention is usually a tank with a stirrer, but a stirrer is not required. A bubble tower type may also be adopted. A cooler is installed at the upper part of the reactor, and a port for supplying the gas containing molecular oxygen is installed at the lower part. The gas containing molecular oxygen supplied from the lower part is then utilized in the oxidizing reaction and discharged as a gas component accompanied by a large amount of acetic acid vapor from the reactor, then the acetic acid is condensed and separated by a reflux cooler and discharged as an oxidized exhaust gas. Part of the condensate is purged to the system outside to adjust the moisture, and the rest is refluxed to the reactor.

[0014] In the present invention, when the oxidizing reaction of the alkyl aromatic hydrocarbon is carried out, as described in Japanese Kokai Patent Application No. Hei 9[1997]-278709, an oxidized exhaust gas obtained by condensing and removing a condensable component from the gas discharged from the reactor is branched into two flows. One of them is discharged to the system outside, and the other can be continuously circulated and supplied to the reactor.

[0015] In the present invention, the reaction mixture composed of a reaction medium-aromatic carboxylic acid slurry obtained by oxidizing the alkyl aromatic hydrocarbon in the first oxidation reactor includes an aromatic aldehyde as an impurity. In particular, when terephthalic acid is manufactured using para-xylene as a raw material, the impurity is mainly 4CBA in many cases. In the present invention, in order to reduce the impurities such as aromatic aldehyde, the above-mentioned reaction mixture is transferred to a second oxidizing reaction and subjected to an additional oxidation treatment (hereinafter, referred to as "second oxidation treatment") without supplying the alkyl aromatic hydrocarbon as a raw material. At that time, the reaction mixture supplied to the second oxidizing reaction preferably has a 95% conversion rate of the raw

material alkyl aromatic hydrocarbon into the aromatic carboxylic acid in the oxidizing reaction of the first oxidation reactor.

[0016] The reactor for said second oxidation treatment is usually a stirring tank type similarly to the first oxidation reactor, but no stirrer is necessarily required. A bubble tower type may also be adopted. A reflux cooler is installed at the upper part of the reactor, and a port for supplying the gas containing molecular oxygen is installed at the lower part. The gas containing molecular oxygen supplied from the lower part is utilized in the oxidizing reaction and discharged as a gas component accompanied by a large amount of acetic acid vapor from the reactor, with the acetic acid being condensed and separated by the reflux cooler and discharged as an oxidized exhaust gas.

[0017] As the gas containing molecular oxygen in the second oxidation treatment, air, oxygen diluted with an inert gas, oxygen-enriched air, etc., are used, but air is preferable in terms of facility and cost. The amount of gas containing molecular oxygen supplied is usually about 1/5-1/1,000 of the initial reactants.

[0018] In the present invention, the second oxidizing reaction time is controlled to a specific range. Said second oxidation treatment time shows the average residence time in the second oxidation reactor. The calculated value in which 3,000 is substituted for (B) of the following equation is assumed as the minimum value, and the calculated value in which 1,500 is substituted is assumed as the maximum value.

[0019]

(Expression 3) Second oxidation reactor residence time (min) =  
(purification coefficient)  $\times ((A) - (B)) / (B)$

[0020] Where, (A) represents the aromatic aldehyde content (ppm unit) in the aromatic carboxylic acid crystals in the first oxidation reactor. When (A) is larger than 4,500 ppm, the purification coefficient is 33; when (A) is 3,000-4,500 ppm, the purification coefficient is 50; and when (A) is smaller than 3,000 ppm, the purification coefficient is 100. However, if the value at which 3,000 is substituted for (B) is negative, the minimum value of the second oxidation reactor residence time is set to 0 min, and if the value at which 1,500 is substituted for (B) is negative, the second oxidizing reaction is not carried out. Also, said residence time means the average residence time of the solid and liquid components in the second oxidation reactor. For example, when terephthalic acid is manufactured by the liquid-phase oxidation of para-xylene in acetic acid, the residence time can be confirmed and controlled by a method similar to that of the first oxidizing reaction.

[0021] The crude aromatic carboxylic acid in the reaction mixture obtained in this manner is usually crystallized, separated from the reaction medium, and subjected to a hydrogenation purification treatment. As the crystallization and separation methods, ordinary methods can be



used, with appropriate methods being selected in accordance with the desired aromatic carboxylic acid.

[0022] As the hydrogenation purification treatment, usually, a method that dissolves the crude aromatic carboxylic acid obtained as a slurry of an aqueous medium by heating and that subjects it to a hydrogenation purification at high temperature and high pressure in the presence of a platinum catalyst (Japanese Kokoku Patent No. Sho 41[1966]-16860), etc., is used, but the treatment is not limited to such.

[0023] The substance after the hydrogenation purification treatment is further crystallized, separated from the reaction medium, and dried, so that a high-purity aromatic carboxylic acid is obtained. As the crystallization and separation methods, ordinary methods can be used, with appropriate methods being selected in accordance with the desired aromatic carboxylic acid.

[0024] The present invention is characterized by the fact that the first oxidizing reaction is carried out under a mild reaction temperature of 140-180°C and the second oxidation treatment is carried out for a specific treatment time (reactor residence time). If the treatment time is too short, a satisfactory second oxidation treatment effect tends to be difficult to obtain. Since the second oxidation treatment in the second reaction zone is an oxidation treatment accompanied by a partial dissolution and a recrystallization of the aromatic carboxylic acid crystals, the purification of the aromatic carboxylic acid crystals is not advanced, even by lengthening the treatment time to a specific level or more, so that the effect of reducing the amount of aromatic aldehyde reaches a certain limit. Furthermore, the longer the treatment time, the greater the increase in the level of acetic acid combustion, which is not preferable.

[0025] If the first oxidizing reaction is carried out under a mild reaction temperature of 140-180°C, the purification effect of the crude aromatic carboxylic acid is easily exerted in the subsequent second oxidation treatment. The reason for this is presumed to be that if the first oxidizing reaction is carried out under said condition, the diameter of aromatic carboxylic acid crystals precipitated from the reaction mixture is smaller than crystals obtained under the conventional reaction temperature of higher than 180°C, so that the surface area per unit volume is increased, thereby easily exerting the purification effect. On the other hand, if the oxidizing reaction is carried out at lower than 140°C, the reactivity is too low, which is not preferable. Thus, in the aromatic carboxylic acid, which is easily affected by the purification effect due to the second oxidation treatment, the aromatic aldehyde concentration of the crystals can be adjusted simply by adjusting the residence time in the subsequent second oxidizing reaction treatment. Thus, if the reaction conditions are adjusted, the combustion loss of the reaction medium is greatly reduced, compared with the case wherein only the first oxidizing reaction is carried out and the reaction conditions are adjusted. The residence time of the second oxidizing

reaction treatment is set as follows in consideration of the amount of aromatic aldehyde contained as an impurity and the allowable range of the amount of loss of the reaction medium.  
[0026]

(Expression 4) Second oxidation reactor residence time (min) =  
(purification coefficient)  $\times ((A) - (B)) / (B)$

[0027] Where, (A) represents the aromatic aldehyde content (ppm units) in the aromatic carboxylic acid crystals in the first oxidation reactor. When (A) is larger than 4,500 ppm, the purification coefficient is 33; when (A) is 3,000-4,500 ppm, the purification coefficient is 50; and when (A) is smaller than 3,000 ppm, the purification coefficient is 100. However, if the value at which 3,000 is substituted for (B) is negative, the minimum value of the second oxidation reactor residence time is set to 0 min, and if the value at which 1,500 is substituted for (B) is negative, the second oxidizing reaction is not carried out.

[0028] The purification coefficient of the above-mentioned equation is changed at three stages in accordance with the aromatic aldehyde content in the aromatic carboxylic acid crystals in the first oxidization reactor. Thus, the easy exertion of the purification effect in the second oxidization reaction of said crystals is reflected on the second oxidation treatment time. Under the condition in which said aromatic aldehyde content is increased, since the diameter of the crystals tends to be decreased, said aromatic aldehyde content becomes a scale for evaluating the case of exerting the purification effect. In other words, if said aromatic aldehyde content is large, the purification coefficient is set to a smaller value.

[0029] The above-mentioned equation is a means that calculates the residence time for giving the desired result of the second oxidation treatment. A desirable aspect of the second oxidation treatment is to allow a certain number of conditions to generally be considered\*. Among the conditions to be considered, the desired amount of aromatic aldehyde contained as an impurity, the upper limit of the amount of reaction medium loss that is economically allowable, the economic efficiency of the second oxidizing reaction treatment itself, etc., can be mentioned.

[0030] In actuality, in the present invention, if the second oxidation treatment time is determined using the above-mentioned equation, the aromatic aldehyde content in the aromatic carboxylic acid after the second oxidation can be controlled to a desirable range, and the amount of reaction medium loss can be suppressed to an economically allowable amount, without lengthening the treatment time in the second oxidizing reaction. Appropriate reaction conditions of the subsequent second oxidizing reaction can be easily determined, simply by quantifying [limiting]

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\* [Possibly meaning that a limited number of conditions only need to be considered in order to obtain the desired results.]

the amount of aromatic aldehyde in the crude aromatic carboxylic acid purified in the first oxidizing reaction.

[0031] Furthermore, in relation to the aromatic aldehyde content in the aromatic carboxylic acid after the second oxidation, if the second oxidation treatment time is controlled in a range obtained by respectively substituting the minimum value (ppm units) and the maximum value (ppm units) of the desired value for (B) of the above-mentioned equation, the desired aromatic aldehyde concentration can be easily obtained.

[0032] Next, the present invention is explained in further detail with application examples; however, the present invention is not limited to these application examples unless its essence is deviated. Also, "parts" indicates "parts by weight," and "ppm" indicates "wt ppm."

[0033]

#### Application examples

Using the methods shown in each experimental example, terephthalic acid was manufactured using para-xylene as a raw material.

#### Experimental Example 1

A reaction was carried out using a continuous-reaction apparatus consisting of (A) a first oxidation reactor made of titanium equipped with reflux cooler, stirrer, catalyst, solvent and para-xylene supply line, oxygen-containing gas introduction line, reaction slurry discharge line, reflux solution discharge line, and oxidized exhaust gas line, (B) a second oxidation reactor made of titanium equipped with a reflux cooler, stirrer, oxygen-containing gas introduction line, and reaction slurry inlet and outlet, and (C) a crystallizer equipped with a reflux cooler, stirrer, and reaction slurry inlet and outlet. A mixture composed of 1 part para-xylene, 4.6 parts acetic acid containing 5% water, 0.095 part cobalt acetate-tetrahydrate, 0.0003 part manganese acetate-tetrahydrate, 0.0072 part hydrobromic acid (47% aqueous solution), and 0.0004 part sodium hydroxide was supplied at 5.617 parts/h (when the concentration of each catalyst component in the reactor was calculated, cobalt (Co) was 1,000 ppm, manganese (Mn) was 30 ppm, bromine (Br) was 1,500 ppm, and sodium (Na) was 100 ppm) to the first oxidation reactor. Also, the moisture concentration in the reaction system was adjusted to about 10% by discharging the reflux solution at 1.6 parts/h, and the oxidizing reaction of the para-xylene was carried out under the conditions of a reaction temperature of 175°C, a reaction pressure of 1.38 MPa, and a residence time of 100 min. The amount of air was adjusted so that the oxygen concentration in the oxidized exhaust gas was 6 vol%. The reaction slurry was then discharged from the first oxidation reactor, and the slurry was continuously sent to the second oxidation reactor. Air was supplied under the conditions of a reaction temperature of 175°C and a residence time of respectively 30 min, 54 min, and 77 min, so that the oxygen concentration in the second oxidized exhaust gas was 6 vol%, and the second oxidation was carried out. The

second oxidation reactor was always maintained at a pressure 0.15 MPa lower than that of the first oxidation reactor. After the second oxidation, the reaction slurry was continuously sent to the crystallizer, crystallized, subjected to a solid-liquid separation, and dried, so that terephthalic acid crystals were obtained. After applying such a continuous reaction for 24 h, the terephthalic acid crystals obtained were analyzed; as a result, only 4CBA was detected as the aromatic aldehyde. The 4CBA content of the crystals and the amount of acetic acid solvent combusted during the manufacture are shown in Table I.

[0034]

(Table I)

Experiment No.	1-1	1-2	1-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	1000/30/1500	←	←	(ppm)
Reaction temperature	175	←	←	(°C)
Reaction pressure	1.38	←	←	(MPa)
Residence time	100	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.75	←	←	
4CBA concentration in the cake after the first oxidizing reaction	3816	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	175	←	←	(°C)
Residence time	30	54	77	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.06	0.09	0.12	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	0.81	0.84	0.87	
4CBA concentration in the cake after the second oxidizing reaction	2402	1928	1556	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	20	16	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	14~77	←	←	(min)
	Application example	Application example	Application example	

[0035] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)

[0036] Experimental Examples 2-8

Reactions were carried out by a method similar to that of Experimental Example 1, except for changing the reaction conditions of the first oxidizing reaction and the second oxidizing reaction as shown in Tables II-VIII. When the terephthalic acid crystals obtained were analyzed, only 4CBA was detected as the aromatic aldehyde in all of the experimental examples. The results are shown in Tables II-VIII.

[0037]

(Table II)

Experiment No.	2-1	2-2	2-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	1000/30/1500	←	←	(ppm)
Reaction temperature	175	←	←	(°C)
Reaction pressure	1.38	←	←	(MPa)
Residence time	120	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.82	←	←	
4CBA concentration in the cake after the first oxidizing reaction	2529	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	175	←	←	(°C)
Residence time	30	54	77	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.06	0.08	0.09	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	0.88	0.90	0.91	
4CBA concentration in the cake after the second oxidizing reaction	1936	1660	1430	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	12	10	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	0~69	←	←	(min)
	Application example	Application example	Comparative example	

[0038] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)

[0039]

(Table III)

Experiment No.	3-1	3-2	3-3	3-4	
First oxidizing reaction conditions					
Catalyst concentration (Co/Mn/Br)	1000/30/1500	←	←	←	(ppm)
Reaction temperature	170	←	←	←	(°C)
Reaction pressure	1.28	←	←	←	(MPa)
Residence time	100	←	←	←	(min)
First oxidizing reaction results					
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.62	←	←	←	
4CBA concentration in the cake after the first oxidizing reaction	5601	←	←	←	(ppm)
Second oxidizing reaction conditions (**)					
Reaction temperature	170	←	←	←	(°C)
Residence time	30	54	77	95	(min)
Second oxidizing reaction results					
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.06	0.09	0.11	0.21	
Relative value of the amount of acetic acid combusted (*)					
Total of the first and second oxidizing reactions	0.68	0.71	0.73	0.83	
4CBA concentration in the cake after the second oxidizing reaction	3012	1989	1640	1612	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	43	15	2	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	29~90	←	←	←	(min)
	Application example	Application example	Application example	Comparative example	

[0040] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)

[0041]

(Table IV)

Experiment No.	4-1	4-2	4-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	1000/30/1500	←	←	(ppm)
Reaction temperature	170	←	←	(°C)
Reaction pressure	1.28	←	←	(MPa)
Residence time	120	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.68	←	←	
4CBA concentration in the cake after the first oxidizing reaction	4889	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	170	←	←	(°C)
Residence time	30	54	77	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.06	0.08	0.09	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	0.74	0.76	0.77	
4CBA concentration in the cake after the second oxidizing reaction	2332	1681	1421	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	27	11	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	21~75	←	←	(min)
	Application example	Application example	Comparative example	

[0042] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)

[0043]

(Table V)

Experiment No.	5-1	5-2	5-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	1000/30/1500	←	←	(ppm)
Reaction temperature	165	←	←	(°C)
Reaction pressure	1.15	←	←	(MPa)
Residence time	150	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.62	←	←	
4CBA concentration in the cake after the first oxidizing reaction	5261	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	165	←	←	(°C)
Residence time	54	77	100	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.05	0.08	0.11	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	0.67	0.70	0.73	
4CBA concentration in the cake after the second oxidizing reaction	2061	1550	1404	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	22	6	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	25~83	←	←	(min)
	Application example	Application example	Comparative example	

[0044] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)



[0045]

(Table VI)

Experiment No.	6-1	6-2	
First oxidizing reaction conditions			
Catalyst concentration (Co/Mn/Br)	1200/36/1800	←	(ppm)
Reaction temperature	155	←	(°C)
Reaction pressure	0.84	←	(MPa)
Residence time	150	←	(min)
First oxidizing reaction results			
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.42	←	
4CBA concentration in the cake after the first oxidizing reaction	10465	←	(ppm)
Second oxidizing reaction conditions (**)			
Reaction temperature	155	←	(°C)
Residence time	77	100	(min)
Second oxidizing reaction results			
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.07	0.10	
Relative value of the amount of acetic acid combusted (*)			
Total of the first and second oxidizing reactions	0.49	0.52	
4CBA concentration in the cake after the second oxidizing reaction	3140	2050	(ppm)
Residence time extension effect in the second oxidizing reaction (***)	—	47	(ppm/min)
Second oxidizing reaction residence time attained by the method shown in Claim 1	82~197	←	(min)
	Comparative example	Application example	

[0046] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

(\*\*\*) The effect of the second oxidation treatment time extension on the reduction of the amount of 4CBA (the value in which the amount difference of the 4CBA from the left adjacent column is divided by the residence time difference from the left adjacent column)

[0047]

(Table VII)

Experiment No.	7-1	7-2	7-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	650/20/975	←	←	(ppm)
Reaction temperature	190	←	←	(°C)
Reaction pressure	1.94	←	←	(MPa)
Residence time	100	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	1.00	←	←	
4CBA concentration in the cake after the first oxidizing reaction	3420	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	190	←	←	(°C)
Residence time	30	54	77	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.15	0.18	0.21	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	1.15	1.18	1.21	
4CBA concentration in the cake after the second oxidizing reaction	2662	2222	1981	(ppm)
Second oxidizing reaction residence time attained by the method shown in Claim 1	7~64	←	←	(min)
	Comparative example	Comparative example	Comparative example	

[0048] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

[0049]

(Table VIII)

Experiment No.	8-1	8-2	8-3	
First oxidizing reaction conditions				
Catalyst concentration (Co/Mn/Br)	800/24/1200	←	←	(ppm)
Reaction temperature	185	←	←	(°C)
Reaction pressure	1.77	←	←	(MPa)
Residence time	100	←	←	(min)
First oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the first oxidizing reaction (*)	0.95	←	←	
4CBA concentration in the cake after the first oxidizing reaction	3110	←	←	(ppm)
Second oxidizing reaction conditions (**)				
Reaction temperature	185	←	←	(°C)
Residence time	30	54	77	(min)
Second oxidizing reaction results				
Relative value of the amount of acetic acid combusted in the second oxidizing reaction (*)	0.14	0.17	0.22	
Relative value of the amount of acetic acid combusted (*)				
Total of the first and second oxidizing reactions	1.09	1.12	1.17	
4CBA concentration in the cake after the second oxidizing reaction	2499	2121	1859	(ppm)
Second oxidizing reaction residence time attained by the method shown in Claim 1	2~54	←	←	(min)
	Comparative example	Comparative example	Comparative example	

[0050] (\*) The relative value of the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7

(\*\*) The reaction pressure is 0.15 MPa lower than that of the first oxidizing reaction.

[0051] Experimental Example 9

Similarly to Experimental Example 1, except for setting the catalyst concentration to twice the previous amount, the reaction temperature to 130°C, the reaction pressure to 0.41 MPa, and the residence time to 150 min, the first oxidizing reaction was carried out. As a result, since the reactivity was too low, a stable continuous reaction could not be carried out.

[0052] As shown in Experimental Examples 7 and 8, in the crude terephthalic acid crystals obtained at a reaction temperature of 185°C or higher in the first oxidizing reaction, the amount

of acetic acid combusted in the first oxidation reactor was increased, compared with the other experimental examples. Also, when the second oxidation reactor residence time was extended, the change in the 4CBA content in the crude terephthalic acid crystals in the second oxidation reactor was small. Also, as shown in Experimental Example 9, the reactivity was considerably low at a reaction temperature of 130°C, and a stable reaction was impossible.

[0053] In Experimental Examples 1-6 in which the reaction temperature of the first reactor was set to 140-180°C, when the second oxidation treatment time was set to the range of the equation shown in Claim 1, the second oxidizing reaction simultaneously resulted in the following:

- (1) The 4CBA content of the terephthalic acid crystals after the second oxidation treatment is controlled to a range of 1,500-3,000 ppm.
- (2) The amount of acetic acid lost by the combustion in the first oxidizing reaction and the second oxidizing reaction is a relative value when the amount of acetic acid lost in the first oxidizing reaction of Experimental Example 7 is assumed as 1, and the amount is suppressed to 0.13 or less.
- (3) The effect of the extension of the second oxidation treatment time on the reduction of the amount of 4CBA (the value in which the difference in the amount of 4CBA is divided by the difference of the residence time, compared with the experimental data in which the second oxidation treatment time is as short as 13-24 min) is maintained at 12 ppm/min or more.

[0054]

#### Effects of the invention

According to the present invention, in the method for manufacturing an aromatic carboxylic acid by subjecting an alkyl aromatic hydrocarbon to a liquid-phase oxidation using a gas containing molecular oxygen, aromatic carboxylic acid crystals in which the aromatic aldehyde content is controlled to a desirable range can be obtained while suppressing the amount of reaction medium being lost. Also, based on the amount of aromatic aldehyde included in crude aromatic carboxylic acid crystals after the first oxidizing reaction, the reaction conditions of the subsequent second oxidizing reaction can be simply determined.